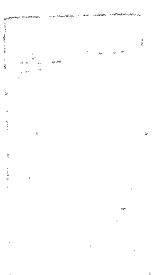


POLYMER CHEMISTRY

An Introduction

SECOND EDITION

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Apart from some limited applications with styrene, thermal polymerization has been used commercially only with certain polymers or oligomers end-capped with thermally labile moieties such as maleimide or nadimide for manufacture of composites (see Chapter 4, Table 4.4).

6.3 Techniques of free radical polymerization

Free radical polymerization can be accomplished in bulk, suspension, solution, or emulsion. Free radical polymerizations are usually confined to solution techniques. Each of the methods has advantages and disadvantages, as outlined in Table 6.2. In addition, work has also been done on solid- and gas-phase polymerizations of vinyl monomers, but these are of lesser importance. Because polymers are not volatile, the term *gas-phase polymerization* means, in effect, bulk polymerization in which monomer vapors diffuse to the polymerization site. A special case of solid-phase polymerization involving inclusion complexes is discussed in Section 6.6.

6.3.1 Bulk

Bulk polymerization is simplest from the standpoint of formulation and equipment, but it is also the most difficult to control, particularly when the polymerization reaction is very exothermic. This, coupled with problems of heat transfer as the monomer-polymer solution increases in viscosity, limits the use of bulk methods in commercial production, although more efficient bulk processes have been developed in recent years.

In cases where polymer is insoluble in monomer, polymer precipitates and the viscosity of the medium does not change appreciably. Problems still arise, however, as a result of free radicals (detectable by ESR) being occluded in the polymer droplet, which can lead to *autoacceleration*, that is, a rapid increase in the polymerization rate.¹³ In some instances, particularly with diene monomers, this occlusion effect may lead to formation of insoluble crosslinked polymer nodules, a phenomenon referred to as *popcorn polymerization*.¹⁴ The crosslinked nodules are usually of light weight and occupy considerably more volume than the monomers from which they are derived, which may cause fouling and even fracture of the polymerization apparatus.

Table 6.2. Free radical polymerization techniques

Method	Advantages	Disadvantages
Bulk	Simple; no contaminants added	Reaction exotherm difficult to control; high viscosity
Suspension	Heat readily dispersed; low viscosity; polymer obtained in granular form and may be used directly	Washing and/or drying required; agglomeration may occur; contamination by stabilizer
Solution	Heat readily dispersed; low viscosity; may be used directly as solution	Added cost of solvent; solvent difficult to remove; possible chain transfer with solvent; possible environmental pollution
Emulsion	Heat readily dispersed; low viscosity; high molecular weight obtainable; may be used directly as emulsion; works on tacky polymers	Contamination by emulsifier and other ingredients; chain transfer agents often needed to control DP; washing and drying necessary for bulk polymer

The major commercial uses of bulk vinyl polymerization are in casting formulations and low-molecular-weight polymers for use as adhesives, plasticizers, tackifiers, and lubricant additives.

6.3.2 Suspension

Suspension polymerization involves mechanically dispersing monomer in a noncompatible liquid, usually water, and polymerizing the resultant monomer droplets by use of a monomer-soluble initiator. Monomer is kept in suspension by continuous agitation and the use of *stabilizers*, such as poly(vinyl alcohol) or methyl cellulose. If the process is carefully controlled, polymer is obtained in the form of granular beads, which are easy to handle and can be isolated by filtration or by spraying into a heated chamber (*spray drying*). A major advantage is that heat transfer is very efficient and the reaction is therefore easily controlled. Suspension polymerization cannot be used for tacky polymers such as elastomers because of the tendency for agglomeration of polymer particles. From the standpoint of kinetics and mechanism, suspension polymerization is identical to bulk polymerization. Suspension methods are used to prepare a number of granular polymers, including polystyrene, poly(vinyl chloride), and poly(methyl methacrylate).

6.3.3 Solution

Like suspension, solution polymerization allows efficient heat transfer. Solvent must be chosen carefully, otherwise chain transfer reactions (discussed in

the next section) may severely limit the molecular weight. Because of problems in removing solvent completely from the resultant polymer, the method is best suited to applications where the solution may be used directly, as with certain adhesives or solvent-based paints.

6.3.4 Emulsion

Developed at Goodyear Tire and Rubber Company in the 1920s, emulsion polymerization resembles suspension polymerization in that water is used as a dispersing medium and heat transfer is very efficient, but there the similarity ends.¹⁵⁻¹⁶ Monomer is dispersed in the aqueous phase by an emulsifying agent such as a soap or detergent. Initiator radicals, usually of the redox type, are generated in the aqueous phase and diffuse into soap micelles swollen with monomer molecules. As monomer is used up in the polymerization reaction, more monomer migrates into the micelles, and thus the reaction continues. Termination of polymerization occurs by radical combination when a new radical diffuses into the micelle. Because only one radical is present in the micelle prior to termination, extremely high molecular weights are obtainable, generally too high to be of practical value unless compounds called *chain transfer agents* are added that control the degree of polymerization. (How chain transfer agents work is discussed later in the chapter.) The

Table 6.3. Typical emulsion polymerization recipes^a

Ingredients, conditions	Styrene-butadiene copolymer	Polyacrylate latex
Ingredients (parts by weight)		
Water	190	133
Butadiene	70	—
Styrene	30	—
Ethyl acrylate	—	93
2-Chloroethyl vinyl ether	—	5
<i>p</i> -Divinylbenzene	—	2
Soap	5	3 ^b
Potassium persulfate	0.3	1
<i>n</i> -Dodecyl mercaptan	0.5	—
Sodium pyrophosphate	—	0.7
Conditions		
Time	12 hr	8 hr
Temperature	50°C	60°C
Yield	65%	~100%

^a Recipes from Cooper.^{17a}

^b Sodium lauryl sulfate.

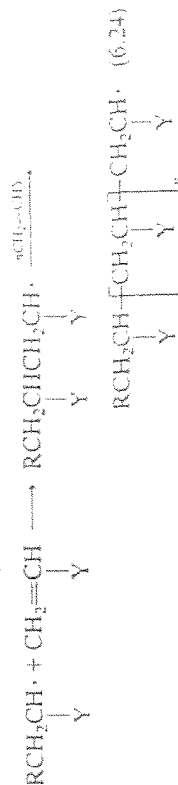
overall process is complex, with reaction kinetics differing significantly from that of bulk or solution processes.

Emulsion polymerization is widely used in industry for large-scale preparations, and is particularly useful for manufacturing water-based (latex) paints or adhesives in which the emulsified product is used directly. Emulsion polymerization is also suitable for preparing tacky polymers because the very small particles are able to resist agglomeration. Two typical emulsion recipes are given in Table 6.3.

A much less commonly used emulsion technique involves dispersing an aqueous solution of monomer in a nonaqueous phase. This is referred to as an *inverse* or *water-in-oil* emulsion (as opposed to the more conventional *oil-in-water* type). The mechanism of polymerization is similar for the two techniques, but inverse emulsions tend to be less stable.

6.4 Kinetics and mechanism of polymerization

Initiation of free radical chain polymerization involves two reactions: formation of the initiator radical (6.22), and addition of the initiator radical to monomer (6.23). Evidence for the incorporation of initiator radicals arises from spectroscopic and chemical analysis of end groups. Addition of monomer radical to another monomer molecule, followed by successive additions of oligomer and polymer radicals to available monomer (6.24), comprise the propagation reactions.



It was mentioned in Chapter 3 (Section 3.5) that each addition step follows the predominant *head-to-tail* orientation shown in reaction (6.24). This is due to a combination of steric and electronic effects. Steric repulsion favors attack by the radical at the least hindered carbon of the double bond; and resonance stabilization favors formation of the more stable free radical. Head-to-tail polymerization does not occur exclusively. Significant amounts of *head-to-head* structures have been found (by ¹⁹F NMR spectroscopy) to occur in certain fluorine-containing polymers, notably poly(vinyl fluoride) (13) and